

Four-membered rings in silica and aluminosilicate glasses

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ABSTRACT

Assignment of the peaks near 485 cm^{-1} in vibrational spectra of $\text{SiO}_2\text{-M}_{1/n}^+\text{AlO}_2$ (where M = an alkali or alkaline earth element) glasses to $\nu_s(\text{T-O-T})$ modes in four-membered rings was tested with molecular orbital calculations. Potential energy minima of cyclic $(\text{H}_8\text{Si}_m\text{Al}_n\text{O}_{12})^{n-}$ (where $m + n = 4$), $\text{Li}_2\text{H}_8\text{Si}_2\text{Al}_2\text{O}_{12}$, $\text{Mg}_2\text{H}_8\text{Al}_4\text{O}_{12}$, $(\text{H}_6\text{Si}_2\text{AlO}_9)^{1-}$, and $\text{LiH}_6\text{Si}_2\text{AlO}_9$ molecules were calculated. Force-constant analyses of the potential-energy-minimized structures predict $\nu_s(\text{T-O-T})$ modes between 490 and 430 cm^{-1} depending on the number of Al atoms in the negatively charged four-membered rings and $\nu_s(\text{T-O-T})$ modes at 525 and 545 cm^{-1} in $\text{Li}_2\text{H}_8\text{Si}_2\text{Al}_2\text{O}_{12}$ and $\text{Mg}_2\text{H}_8\text{Al}_4\text{O}_{12}$, respectively. The theoretical frequency shift of the $\nu_s(\text{T-O-T})$ mode calculated for the $(\text{H}_8\text{Si}_m\text{Al}_n\text{O}_{12})^{n-}$ rings is consistent with the experimentally observed shifts of the peaks at $495\text{--}485$ and $495\text{--}515\text{ cm}^{-1}$ in glasses along the $\text{SiO}_2\text{-NaAlSiO}_4$ and $\text{SiO}_2\text{-CaAl}_2\text{Si}_2\text{O}_8$ joins, respectively (McMillan et al. 1982; Seifert et al. 1982). Force-constant analyses of $(\text{H}_6\text{Si}_2\text{AlO}_9)^{1-}$ and $\text{LiH}_6\text{Si}_2\text{AlO}_9$ molecules predict a frequency of 573 cm^{-1} for the $\nu_s(\text{T-O-T})$ mode in both molecules, consistent with the assignment of peaks near 600 cm^{-1} in glasses along these joins to $\nu_s(\text{T-O-T})$ modes in three-membered rings (McKeown et al. 1984; Kubicki and Sykes 1993a). Intermediate-range order in $\text{SiO}_2\text{-M}_{1/n}^+\text{AlO}_2$ glasses is interpreted in terms of changes in ring statistics. In SiO_2 , the Raman peaks at 606 (D_2), 495 (D_1), and 430 cm^{-1} correspond to three-, four-, and $>$ four-membered rings, respectively. The predominant low-frequency peaks in the vibrational spectra of glasses along the $\text{SiO}_2\text{-NaAlSiO}_4$ and $\text{SiO}_2\text{-CaAl}_2\text{Si}_2\text{O}_8$ joins at $540\text{--}606$ and $485\text{--}515\text{ cm}^{-1}$ are ascribed to three- and four-membered rings, respectively.

INTRODUCTION

Structural models of fully polymerized silica, alkali aluminosilicate, and alkaline earth aluminosilicate glasses are commonly based on an interconnected network of corner-shared silicate and aluminate tetrahedra. However, there is little agreement on the nature of the intermediate-range structural features. Disagreement generally concerns the assignment of low-frequency bands in the vibrational spectra of aluminosilicate glasses (Bates et al. 1974; Sharma et al. 1978; McMillan et al. 1982; Seifert et al. 1982; Revesz and Walrafen 1983; Garofalini 1984; Sharma et al. 1985; Humbert et al. 1992). Silica glass has three low-frequency bands at 430 , 495 (D_1), and 606 (D_2) cm^{-1} . D_1 and D_2 have been interpreted as symmetric

stretching modes of Si-O-Si linkages in four- and three-membered rings of tetrahedra (Galeener et al. 1984; Barrio et al. 1993), broken Si-O bonds (Bates et al. 1974; Sharma et al. 1981; Humbert et al. 1992), and overcoordinated Si and O (Garofalini 1984). Along the $\text{SiO}_2\text{-NaAlSiO}_4$ join, the frequencies of the bands at 495 and 606 cm^{-1} decrease to 485 and 560 cm^{-1} with the addition of NaAlO_2 . Simultaneously, the relative intensities of these bands increase up to the NaAlSiO_4 composition (Seifert et al. 1982). McKeown et al. (1984) suggested that the 495 and 595 cm^{-1} bands in the spectra of $\text{NaAlSi}_3\text{O}_8$ glass correspond to the D_1 and D_2 "defect" bands in vitreous silica at 495 and 606 cm^{-1} , respectively. Alternatively, McMillan et al. (1982) assigned the three low-frequency bands in glasses along this join to $\nu_s(\text{Si-O-Si})$, $\nu_s(\text{Si-O-Al})$, and $\nu_s(\text{Al-O-Al})$ vibrational modes, respectively. Seifert et al. (1982) interpreted the Raman spectra of $\text{SiO}_2\text{-M}_{1/n}^+\text{AlO}_2$ glasses in terms of Si_6 , Al_6 , and Si_2Al_2 rings.

Kubicki and Sykes (1993a) tested Galeener and co-workers' (Galeener 1982a, 1982b; Galeener and Mikkelsen 1981; Galeener and Geissberger 1983; Galeener et al. 1984; Barrio et al. 1993) assignment of the D_2 band in the Raman spectrum of silica to O_{br} (O atoms bonded to

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TABLE 1. Distances (Å), angles (°), energies (Hartrees), and O_{br} breathing-mode frequencies (cm^{-1}) of the Si_2Al and $(\text{Si},\text{Al})_4$ aluminosilicate rings from molecular orbital calculations

Molecule	$(\text{H}_6\text{Si}_2\text{AlO}_6)^{-}$	$(\text{H}_6\text{Si}_4\text{O}_{12})$	$(\text{H}_6\text{Si}_6\text{AlO}_{12})^{-}$	$(\text{H}_6\text{Si}_2\text{Al}_2\text{O}_{12})^{2-}$	$(\text{H}_6\text{SiAl}_3\text{O}_{12})^{3-}$	$(\text{H}_6\text{Al}_4\text{O}_{12})^{4-}$
Energy	-1489.9605	-2049.0226	-2002.2459	-1955.3420	-1908.2609	-1861.0620
$\nu_s(\text{T-O-T})$	574	490	488	483	464	430
Si-O_{br}	(1.614)	(1.623)	(1.614)	(1.609)	(1.604)	—
Si-O_{nbr}	(1.637)	(1.617)	(1.633)	(1.651)	(1.662)	—
Al-O_{br}	(1.761)	—	(1.747)	(1.740)	(1.739)	(1.735)
Al-O_{nbr}	(1.738)	—	(1.747)	(1.764)	(1.787)	(1.807)
$(\text{Si})\text{O-H}$	(0.962)	(0.962)	(0.968)	(0.975)	(0.979)	—
$(\text{Al})\text{O-H}$	(0.964)	—	(0.962)	(0.961)	(0.970)	(0.973)
$O_{br}\text{-Si-O}_{br}$	(107.48)	(108.62)	(111.01)	(112.66)	114.53	—
$O_{nbr}\text{-Si-O}_{br}$	(111.01)	(108.98)	(108.86)	(108.99)	(108.85)	—
$O_{nbr}\text{-Si-O}_{nbr}$	(107.04)	(112.21)	(110.21)	(108.08)	106.70	—
$O_{br}\text{-Al-O}_{br}$	103.13	—	109.34	(113.12)	(114.86)	(117.29)
$O_{nbr}\text{-Al-O}_{br}$	(109.47)	—	(108.31)	(107.88)	(108.01)	(107.95)
$O_{nbr}\text{-Al-O}_{nbr}$	113.70	—	113.85	(111.88)	(109.39)	(107.05)
$\text{Si-O}_{br}\text{-Si}$	132.00	(143.83)	(141.79)	—	—	—
$\text{Si-O}_{br}\text{-Al}$	(130.62)	—	(137.79)	(135.74)	(135.88)	—
$\text{Al-O}_{br}\text{-Al}$	—	—	—	—	(133.66)	(134.40)
Si-O-H	(118.38)	(124.90)	(118.03)	(112.20)	(109.31)	—
Al-O-H	(118.06)	—	(121.13)	(115.07)	(106.94)	(102.43)

Note: Numbers in angle brackets are average values.

two tetrahedral cations) "breathing" modes in three-membered silicate rings and found that molecular orbital calculations on cyclic $\text{H}_6\text{Si}_3\text{O}_6$ accurately reproduce the frequency of the D_2 band in vitreous silica. Thus, the molecular orbital calculations for both $\text{H}_6\text{Si}_3\text{O}_6$ and $\text{H}_6\text{Si}_3\text{O}_3$ (O'Keeffe and Gibbs 1984) are consistent with assignment of the D_2 band to breathing modes in three-membered rings. Because the frequencies calculated for O_{br} breathing modes in aluminosilicate three-membered rings are in similar agreement with the observed vibrational spectra of sodium aluminosilicate glasses, Kubicki and Sykes (1993a) assigned the 540–600 cm^{-1} bands in the Raman spectra of the alkali and alkaline earth aluminosilicate glasses to O_{br} breathing modes in three-membered aluminosilicate rings.

In this paper, we test the assignment of the 485–515 cm^{-1} peaks to O_{br} breathing modes in four-membered rings of aluminate and silicate tetrahedra by comparing theoretical frequencies of cyclic $(\text{H}_6\text{Si}_m\text{Al}_n\text{O}_{12})^{n-}$ molecules with the Raman spectra of silica and $\text{SiO}_2\text{-M}_{n+}^+\text{AlO}_2$ glasses. Similar models, based on the coupling of two four-membered rings to form the double four-membered-ring structure D4R, are often used in the study of zeolite vibrational spectra (e.g., Creighton et al. 1994; Bartsch et al. 1994; Sauer and Hill 1994). Because $\nu_s(\text{T-O-T})$ modes (i.e., the breathing mode in a regular ring structure) in zeolites with four-membered rings occur over the frequency range 486–521 cm^{-1} (Dutta et al. 1991), it is reasonable to expect that similar structures in glasses may produce frequencies in the same range. Furthermore, the anomalously narrow bandwidth of the D_1 peak in vitreous silica is evidence that a fairly regular structure causes this controversial peak (Galeener 1982a, 1982b). The nature of the small molecular rings can help constrain these species to fairly regular structural conformations

even in glasses. Hence, we modeled the intermediate-range structure of glasses with molecules comparable to the structures presumed to be present in the glasses.

METHODS

Minimum potential energy structures and vibrational modes of aluminosilicate rings were calculated using self-consistent, Hartree-Fock molecular orbital calculations with 3-21G(*) basis sets (G = Gaussian functions, approximate Slater-type atomic orbitals; 3-21 = 3 Gaussians per atomic orbital with the valence electrons represented with double-zeta Gaussians; * = d orbitals used as polarization functions on second-row atoms). Calculations were performed with the GAUSSIAN 92 program (Frisch et al. 1992). No symmetry constraints were placed on any of the molecules; $3N - 6$ (where N = number of atoms) structural parameters of each molecule were allowed to vary independently to allow for full optimizations. For molecules with charge-balancing cations (i.e., Li^+ and Mg^{2+}), the charge-balancing cations were initially placed in the center of the ring directly above or below the plane of the ring to allow the cation(s) to interact with the greatest possible number of O atoms and to follow the most energetically favorable interactions. Stationary points were found to be true minima (although not necessarily global minima) of the molecular potential energy surface through force-constant analyses. All reported frequencies were scaled by 0.893 to correct for anharmonicity in the calculated harmonic frequencies, dissociation-limit errors in HF calculations, and the limitations of the 3-21G(*) basis set (Pople et al. 1981). Potential energies were corrected with zero-point energies (ZPE) determined in the force-constant analysis.

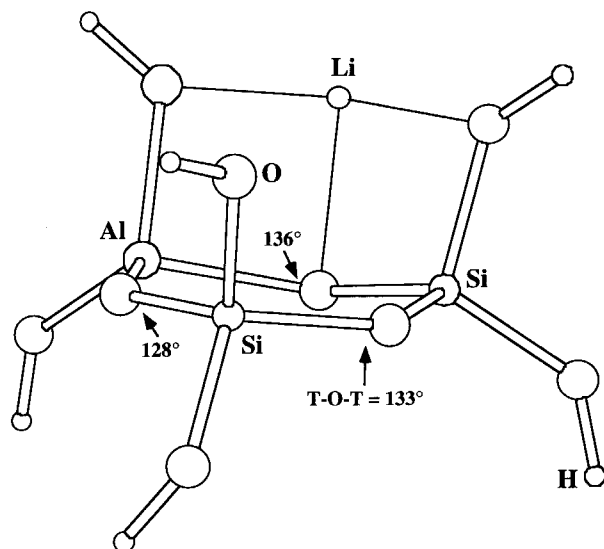


FIGURE 1. Minimum potential energy structure of $\text{LiH}_6\text{Si}_2\text{AlO}_9$ from molecular orbital calculations with a 3-21G(*) basis set. The $\nu_3(\text{T-O-T})$ mode at 574 cm^{-1} is an O_{br} breathing mode similar to the $\nu_3(\text{T-O-T})$ modes of the other three-membered rings reported by Kubicki and Sykes (1993a). Figure drawn with the program ATOMS (Dowty 1991).

RESULTS

Optimized structures

An optimized $(\text{H}_6\text{Si}_2\text{AlO}_9)^{-}$ (hereafter denoted as Si_2Al) structure (Table 1) is similar to that reported by Kubicki and Sykes (1993a) for the partially optimized molecule. Thus, the structural trends discussed in that paper for the three-membered rings as a function of composition remain valid. The ΔE between the fully optimized Si_2Al ring and that reported previously is only -0.03 kJ/mol before the ZPE correction is applied. The molecular structure of an Li^+ charge-balanced Si_2Al ring is pictured in Figure 1. Addition of Li^+ to charge balance the molecule has little effect on the ring structure (Table 2) even though Li^+ forms bonds to three O atoms (Fig. 1). Average Si-O, Al-O, and O-H bond distances are equal to within $<0.007\text{ \AA}$ between the negatively charged and neutral rings. Similarly, the calculated T-O-T and O-T-O angles (T = Si or Al) agree to within 2° between the two molecules. The average Si-O-H and Al-O-H angles in the Li^+ charge-balanced ring are $7\text{--}13^\circ$ larger than in the negatively charged ring.

Structural parameters and potential energies (corrected for ZPE) of the fully optimized $(\text{Si}_m\text{Al}_n\text{O}_{12})^{n-}$ molecules are nonplanar rings with one set of opposing T-O-T angles typically $138\text{--}148^\circ$ and the other set of opposing angles $127\text{--}139^\circ$. Both sets of intertetrahedral angles are approximately 9° smaller in the Al_4 ring than in the Si_4 ring. T- O_{br} bonds associated with

TABLE 2. Distances (\AA), angles ($^\circ$), energies (Hartrees), and O_{br} breathing-mode frequencies (cm^{-1}) of the charge-balanced Si_2Al and $(\text{Si}_m\text{Al}_n)_4$ aluminosilicate rings from molecular orbital calculations

Molecule	$\text{LiH}_6\text{Si}_2\text{AlO}_9$	$\text{Li}_2\text{H}_6\text{Si}_2\text{Al}_2\text{O}_{12}$	$\text{Mg}_2\text{H}_6\text{Al}_4\text{O}_{12}$
Energy	-1497.4568	-1970.4306	-2259.1083
$\nu_3(\text{T-O-T})$	574	526	545
Si-O_{br}	(1.617)	(1.626)	—
Si-O_{nbr}	(1.631)	(1.629)	—
Al-O_{br}	(1.767)	(1.772)	(1.769)
Al-O_{nbr}	(1.735)	(1.732)	(1.753)
(Si)O-H	(0.960)	(1.975)	—
(Al)O-H	(0.957)	(1.958)	(0.958)
$\text{O}_{br}\text{-Si-O}_{br}$	(107.82)	(106.02)	—
$\text{O}_{nbr}\text{-Si-O}_{br}$	(110.16)	(109.32)	—
$\text{O}_{nbr}\text{-Si-O}_{nbr}$	(107.73)	(112.81)	—
$\text{O}_{br}\text{-Al-O}_{br}$	102.21	(99.17)	(95.02)
$\text{O}_{nbr}\text{-Al-O}_{br}$	(109.84)	(110.50)	(110.79)
$\text{O}_{nbr}\text{-Al-O}_{nbr}$	112.34	(113.09)	(113.04)
$\text{Si-O}_{br}\text{-Si}$	133.19	—	—
$\text{Si-O}_{br}\text{-Al}$	(131.69)	(135.70)	—
$\text{Al-O}_{br}\text{-Al}$	—	—	(157.44)
Si-O-H	(125.74)	(122.34)	—
Al-O-H	(130.65)	(130.39)	(129.77)
Li-O	(1.880)	(1.910)	—
Li-O	—	(1.907)	—
MgO1-O	—	—	(1.957)
Mg2-O	—	—	(2.007)

Note: Numbers in angle brackets are average values.

the smaller set of T-O-T angles are longer by $\sim 0.02\text{ \AA}$ than the T- O_{br} bonds associated with the larger set of T-O-T angles. Average Si-O_{br} and Al-O_{br} bond lengths decrease with increasing Al content of the rings, whereas Si-O_{nbr} and Al-O_{nbr} distances increase (Table 1). The average theoretical Si-O_{br} bond lengths of 1.614 and 1.609 \AA for the Si_3Al and the Si_2Al_2 rings, respectively, fall within the range of experimental Si-O_{br} bond lengths of $1.571\text{--}1.647\text{ \AA}$ recorded for natural albite ($\text{NaAlSi}_3\text{O}_8$) and anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$) mineral compositions (Wainwright and Starkey 1971; Kroll and Ribbe 1983). Similarly, the calculated average Al-O_{br} bond lengths of 1.740 \AA in the Si_2Al_2 and 1.735 \AA in the Al_4 rings fall within the range of experimental Al-O_{br} values of $1.698\text{--}1.779\text{ \AA}$ and $1.728\text{--}1.779\text{ \AA}$ recorded for natural $\text{CaAl}_2\text{Si}_2\text{O}_8$ and CaAl_2O_4 mineral compositions, respectively (Horkner and Muller-Buschbaum 1976; Kroll and Ribbe 1983; Muller et al. 1986).

Although all five rings optimized to nonplanar structures, bending the rings into planar geometries does not require a great deal of energy. Potential energies of $\text{H}_8\text{Si}_4\text{O}_{12}$ and $(\text{H}_8\text{Si}_2\text{Al}_2\text{O}_{12})^{2-}$ constrained to planar configurations differ by only -4 and $+39\text{ kJ/mol}$ from the nonplanar configurations. Note that the planar Si_4 ring actually has a slightly lower potential energy than the nonplanar configuration after the ZPE correction has been made, even though the stationary-point energy of the planar configuration is 3 kJ/mol higher than the nonplanar configuration (i.e., the nonplanar ZPE is 7 kJ/mol higher than the planar ZPE).

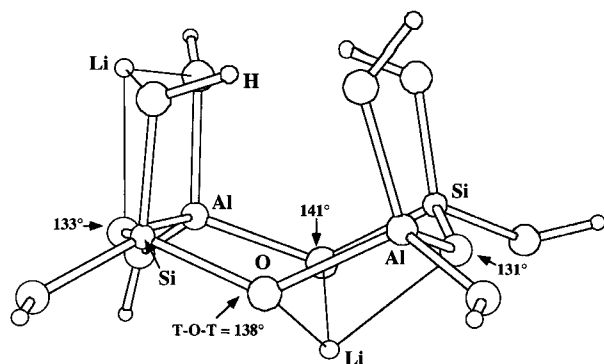


FIGURE 2. Minimum potential energy structure of $\text{Li}_2\text{H}_8\text{Si}_2\text{Al}_2\text{O}_{12}$ from molecular orbital calculations with a 3-21G(*) basis set. The $\nu_s(\text{T-O-T})$ mode at 526 cm^{-1} is an O_{br} breathing mode. The other four-membered rings in this study have similar structures, with bond lengths and angles listed in Tables 1 and 2. Each four-membered ring exhibits a similar vibrational mode. Figure drawn with the program ATOMS (Dowty 1991).

Calculated T-O bond distances of the OH-terminated molecules in this study are comparable to previous experimental (Glidewell et al. 1970) and theoretical (e.g., Chakoumakos et al. 1981; Casewit et al. 1992; Tossell 1993; Hill and Sauer 1994) studies of H-terminated four-membered rings and the T-O bond distances found in crystalline silicates [see Ribbe (1983) for a review]. For example, the gas-phase molecule $\text{H}_8\text{Si}_4\text{O}_4$ has average Si-O bond lengths of 1.628 \AA and Si-O-Si angles of 144.1° (Glidewell et al. 1970) in comparison with 1.623 and 143.8° calculated for our Si_4 ring. Previous theoretical investigations have shown that T-O_{br} bond lengths typically vary $<0.05\text{ \AA}$ as a function of molecular size (e.g., monomer, dimer, etc.), molecular composition (OH- vs. H-terminated), and basis set (e.g., Lasaga and Gibbs 1988; Nicholas et al. 1992). Therefore, the relative agreement between T-O_{br} bond lengths in the OH- and H-terminated $(\text{Si,Al})_4$ molecules is consistent with prior results.

Although T-O_{br} bond distances remain relatively constant between H- and OH-terminated molecules, calculated T-O-T bond angles depend on the type of terminal bond at this level of theory. In molecules of the type $\text{H}_3\text{T-O-T-H}_3$, intertetrahedral angles of the optimized geometries are 180° with 3-21G(*) basis sets (Hill and Sauer 1989). On the other hand, in $(\text{OH})_3\text{T-O-T}(\text{OH})_3$ molecules, optimized T-O-T angles vary between 130 and 150° (Geisinger et al. 1985; Sauer 1989; Nicholas et al. 1992; Kubicki and Sykes 1993b), a range that is more consistent with experimental values in crystals and glasses (Sharma et al. 1988; Geisinger et al. 1985). The above relationship is also observed in larger molecules of the type $(\text{H}_3\text{SiO})_3\text{TOH}$ and $[(\text{OH})_3\text{SiO}]_3\text{TOH}$ (Kubicki and Sykes 1995). Tossell (1993) reported equilibrium bond angles of Si-O-Si = 150° , Si-O-Al = 155.9° , and Al-O-Al = 151°

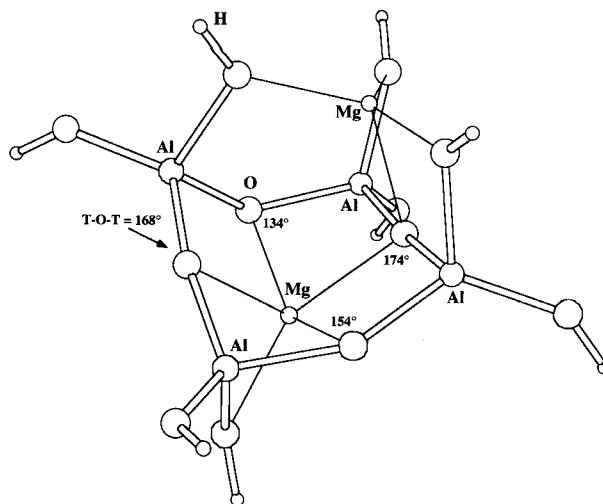


FIGURE 3. Minimum potential energy structure of $\text{Mg}_2\text{H}_8\text{Al}_4\text{O}_{12}$ from molecular orbital calculations with a 3-21G(*) basis set. The $\nu_s(\text{T-O-T})$ mode at 545 cm^{-1} is an O breathing mode, although the ring is highly distorted from a regular geometry in this case. Figure drawn with the program ATOMS (Dowty 1991).

for the cyclic molecules $\text{H}_8\text{Si}_4\text{O}_4$, $(\text{H}_8\text{Si}_2\text{Al}_2\text{O}_4)^{2-}$, and $(\text{H}_8\text{Al}_4\text{O}_4)^{4-}$, respectively. T-O-T angles calculated in the $(\text{H}_8\text{Si}_m\text{Al}_n\text{O}_{12})^{n-}$ molecules are significantly lower (Table 1) and closer to experimental values. The frequencies predicted by Tossell (1993) for the symmetric stretching modes in the $(\text{Si,Al})_4$ rings differ from our own because of the different terminal bonds and T-O-T angles.

The inclusion of two Li^+ cations to charge balance the Si_2Al_2 ring (Fig. 2) significantly influences the optimized geometry of the molecule (Table 2). The average Si-O_{br} and Al-O_{br} distances are larger by 0.017 and 0.032 \AA , respectively, in the Li^+ charge-balanced molecule (Table 2). In contrast, T-O_{br} distances decrease by amounts almost equal to the observed changes in T-O_{br} bond lengths. The average Si-O-Al angle is identical in the two molecules, but the difference in the average T-O-T angle between the smaller set of opposing T-O-T angles (132.2°) and the larger set of opposing T-O-T angles (139.3°) is smaller in the Li^+ charge-balanced ring than in the negatively charged ring (129.6 and 141.9° , respectively).

The addition of two Mg^{2+} cations to the Al_4 ring ($\text{Mg}_2\text{H}_8\text{Al}_4\text{O}_{12}$; Fig. 3) also results in significant changes in the ring structure compared with the negatively charged molecule. The average Al-O_{br} distance increases by 0.034 \AA , whereas the average Al-O_{br} distance decreases by 0.056 \AA (Table 2). Al-O-Al intertetrahedral angles range from 133 to 173° , with the average angle (157°) approximately 23° larger than in the Al_4 ring. The addition of Mg^{2+} for charge balancing results in greater changes than the addition of Li^+ , and this is consistent with experimental and theoretical studies that suggest a larger effect of Mg^{2+}

ions on aluminosilicate frameworks (Titova et al. 1995; Beran 1982).

However, the nature of the bonding between the aluminosilicate framework and either the Li^+ or Mg^{2+} charge-balancing cations is almost purely ionic. Natural bond-orbital analysis (Glendening et al. 1992) reveals no bonds sharing electrons between the four-membered rings and the Li^+ or Mg^{2+} . Only minor charge transfers occur from the T-O bonding and O lone-pair orbitals to the Li^+ and Mg^{2+} lone-pair antibonding orbitals. The largest decrease in charge computed for any O atom in these rings was only 0.1 e for a bridging O atom bonded to a Mg^{2+} ion in the Al_4 ring. Hence, the nature and amount of this electron delocalization are similar to that calculated for hydrogen bonds in weakly interacting molecular complexes in which charge transfer from bonding to antibonding orbitals is thought to occur (Reed et al. 1988).

Frequency analyses

Force-constant analysis of the Si_2Al ring predicts a frequency of 573 cm^{-1} for the O_{br} breathing mode, which is consistent with the predicted trend in Figure 4 derived from the other three-membered aluminosilicate rings (Kubicki and Sykes 1993a). The frequency of the O_{br} breathing mode in the Li^+ charge-balanced Si_2Al ring is also calculated to be 573 cm^{-1} . These results are consistent with a weak interaction between the bridging O atoms and the low-field-strength charge-balancing cations (Roy and Navrotsky 1984) and with the premise that the O_{br} breathing modes in the theoretical, non-charge-balanced, three-membered rings are representative of the O_{br} breathing modes in the three-membered rings in the alkali aluminosilicate glasses (Kubicki and Sykes 1993a). This consistency is observed despite the fact that the Li-O interaction is stronger in the theoretical rings because the Li^+ cation in our optimized geometries is bonded to three O atoms rather than the four O atoms expected in the natural glass compositions on the basis of charge and mass-balance constraints. It might be expected, however, that the frequency of the O_{br} breathing modes in three-membered rings with higher Li and Al contents could diverge from the trend defined by the sodic series in Figure 4 because of the higher field strength and lower coordination state of the Li^+ cation in comparison with that of the Na^+ cation in the aluminosilicate glass compositions.

Force-constant analyses of the optimized $(\text{Si},\text{Al})_4$ ring geometries predict symmetric stretching modes of the bridging O atoms in each of the five molecules. The frequencies of these O_{br} breathing modes range from 490 cm^{-1} in the Si_4 ring to 430 cm^{-1} in the Al_4 ring (Fig. 4). The predicted frequency of the O_{br} breathing mode in the Si_4 ring is within error of the 495 cm^{-1} D_1 band in silica glass. Furthermore, the ^{18}O - ^{16}O frequency shifts of the breathing modes in the Si_4 and Si_2Al_2 rings are -19 and -23 cm^{-1} , respectively. These values are similar to the

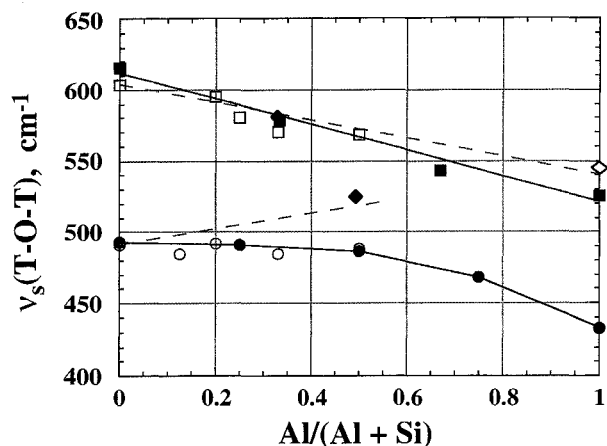


FIGURE 4. Frequencies of O breathing modes calculated for three- and four-membered aluminosilicate rings as a function of $\text{Al}/(\text{Al} + \text{Si})$ ratio. Data represented by open circles and squares are frequencies of the $485\text{--}515$ and $540\text{--}606\text{ cm}^{-1}$ bands, respectively, in alkali aluminosilicate glass compositions (Seifert et al. 1982). Solid circles and squares are frequencies of the O breathing modes for the theoretical three- and four-membered rings, respectively. Solid diamonds are frequencies of the O breathing modes for the Li^+ charge-balanced three- and four-membered rings. The open diamond is the $\nu_s(\text{T-O-T})$ frequency for the Mg^{2+} charge-balanced Al_4 ring. Solid lines are best fits to theoretical points. The dashed lines represent experimental trends of the D_1 and D_2 peaks in $\text{SiO}_2\text{-CaAl}_2\text{O}_4$ glasses.

measured value of -30 cm^{-1} for the ^{18}O - ^{16}O frequency shift of the D_1 peak in silica glass (Galeener and Mikkelsen 1981). Si_4 and Si_2Al_2 planar configurations have breathing-mode frequencies that are 16 and 7 cm^{-1} higher, respectively, than the nonplanar configurations. The correlations between predicted frequencies of O_{br} breathing modes in $(\text{Si},\text{Al})_3$ and $(\text{Si},\text{Al})_4$ rings and the observed frequencies of the $540\text{--}606$ and $485\text{--}515\text{ cm}^{-1}$ peaks as a function of the $\text{Al}/(\text{Al} + \text{Si})$ ratio of the ring or glass (Fig. 4) are evidence that these two bands in $\text{SiO}_2\text{-Na-AlSiO}_4$ glasses result from O_{br} breathing modes in three- and four-membered aluminosilicate rings.

The predicted frequencies of the O_{br} breathing modes in the Si_2Al_2 and Al_4 rings charge balanced by the Li^+ and Mg^{2+} cations are 525 and 545 cm^{-1} , respectively. The frequencies are not consistent with the trend defined by the sodic series but do coincide with the trend for the calcic series (Fig. 4).

DISCUSSION

Assignment of the $540\text{--}606\text{ cm}^{-1}$ peak to (Si,Al) three-membered rings (Kubicki and Sykes 1993a) has important implications for the structural interpretation of aluminosilicate glasses. The observed (Sharma et al. 1978; McMillan et al. 1982; Seifert et al. 1982) and calculated decrease in the frequency of this band with increasing Al

content is evidence against $\nu_s(\text{Si-O-Al})$ vibrations having a higher frequency than $\nu_s(\text{Si-O-Si})$ vibrations. Because substitution of Al for Si tends to narrow T-O-T angles (Sharma et al. 1988) and closure of a given T-O-T angle shifts the $\nu_s(\text{T-O-T})$ vibration to higher frequencies (Furukawa et al. 1981; Kubicki and Sykes 1993b), some authors (e.g., McMillan et al. 1982) have assumed that the frequency of the $\nu_s(\text{T-O-T})$ vibrational mode would increase with Al content similarly to the observed pressure-dependent shift of the $\nu_s(\text{T-O-T})$ vibrational mode with closure of the T-O-T angle in silica and aluminosilicate glasses (McMillan and Graham 1981; McMillan et al. 1984; Hemley et al. 1986). However, Kubicki and Sykes (1993b) noted that substitution of Al for Si in $(\text{OH})_3\text{T-O-T}(\text{OH})_3$ molecules reduces the T-O-T angle, but the frequency of the $\nu_s(\text{T-O-T})$ symmetric stretch decreases because the Al-O_{br} bond is longer than the Si-O_{br} bond. Hence, the compositional effect is not equivalent to the pressure effect where the frequency of the symmetric stretch increases with closure of a given T-O-T linkage.

This same argument can be applied to the assignment of the 495–485 cm^{-1} peaks in alkali aluminosilicate glasses. The addition of NaAlO_2 results in an observed overall increase in the frequency of the peak maximum of the dominant low-frequency peak from 430 cm^{-1} in SiO_2 glass to 485 cm^{-1} in NaAlSiO_4 glass (McMillan et al. 1982; Seifert et al. 1982). Previous interpretations (e.g., McMillan et al. 1982; Seifert et al. 1982) have attributed this behavior to an Si- and Al-dependent shift of the $\nu_s(\text{T-O-T})$ vibrational mode at 430 cm^{-1} to higher frequencies [i.e., $\nu_s(\text{Si-O-Si}) \approx 430 \text{ cm}^{-1}$; $\nu_s(\text{Si-O-Al}) \approx 485 \text{ cm}^{-1}$; $\nu_s(\text{Al-O-Al}) \approx 560 \text{ cm}^{-1}$]. Our results clearly demonstrate, however, that Al decreases the frequency of the $\nu_s(\text{T-O-T})$ vibration, and so the observed apparent increase in the principal low-frequency peak cannot simply be due to a frequency increase of the $\nu_s(\text{T-O-T})$ mode with substitution of Al^{3+} for Si^{4+} .

Instead, the overall increase could be due to an increase in the percentage of four-membered rings and a decrease in the percentage of six-membered rings with increasing NaAlO_2 content of the glass. As the intensity of the band due to the four-membered-ring structural feature increases with NaAlO_2 content, the apparent low-frequency peak maximum increases. This interpretation is consistent with the small decrease in frequency of the $\nu_s(\text{T-O-T})$ mode from 495 cm^{-1} in SiO_2 to 485 cm^{-1} in NaAlSiO_4 , with Al content in the four-membered rings up to an $\text{Al}/(\text{Al} + \text{Si})$ ratio of 0.5 where Si_2Al_2 rings predominate.

The increase in frequency of the D_1 peak in silica to 515 cm^{-1} in $\text{CaAl}_2\text{Si}_2\text{O}_8$ is explicable in terms of several factors. First, bandwidths recorded for the alkaline earth aluminosilicates are typically much broader than those recorded for the alkali aluminosilicates. Therefore, the calculated small shift of the 495 cm^{-1} peak combined with the large frequency decrease and concomitant intensity increase of the 540–606 cm^{-1} shoulder could result

in an apparent positive shift in the 495 cm^{-1} peak from increased band overlap. In addition, mass balance (e.g., one Ca^{2+} charge balances two Al tetrahedra in $\text{CaAl}_2\text{Si}_2\text{O}_8$) imposes constraints on the extended geometry of the glass, which may favor a higher proportion of three-membered rings in the alkaline earth aluminosilicates and lead to increased band overlap. Furthermore, charge-balancing cations with high field strengths (e.g., Ca^{2+}) interact more strongly with the bridging O in Al-O-Si linkages than low-field-strength cations (e.g., Na^+). This polarization of the bridging O weakens the Al-O-Si linkage (Roy and Navrotsky 1984) and results in a smaller observed dependence of the frequency of the symmetric stretching mode on the Al content of the T-O-T linkage or ring (Sharma et al. 1988; Kubicki and Sykes 1993a). In other words, the frequency of the vibrational mode is a function of the Al content and the type of charge-balancing cation. Given the weak Al dependence of the frequency of the O_{br} breathing mode in the $(\text{Si,Al})_4$ rings, the strong interaction between Ca and the bridging O may result in a small increase in the frequency of the vibrational mode as a function of the CaAl_2O_4 content.

As a test of this hypothesis, a force-constant analysis was performed on the $\text{Mg}_2\text{H}_8\text{Al}_4\text{O}_{12}$ molecule. The predicted frequency of the O_{br} breathing mode is 545 cm^{-1} . As is evident from Figure 4, the predicted frequency of the $\text{Mg}_2\text{H}_8\text{Al}_4\text{O}_{12}$ $\nu_s(\text{T-O-T})$ mode is close to the dominant low-frequency peak near 540 cm^{-1} in CaAl_2O_4 glass. Consequently, both Al_3 and Al_4 rings may contribute to the 540 cm^{-1} peak in the calcium aluminate glass spectrum.

The calculated frequency of $\text{Li}_2\text{H}_8\text{Si}_2\text{Al}_2\text{O}_{12}$ is equal to 525 cm^{-1} , which is close to the value of 515 cm^{-1} for a glass with $\text{CaAl}_2\text{Si}_2\text{O}_8$ composition. The similar values between the Li^+ charge-balanced Si_2Al_2 ring and the calcic series may not be altogether fortuitous. Because the field strength of the Li^+ cation is larger than that of Na^+ , it is expected that as the LiAl content of the four-membered rings increases the calculated trend in frequencies for the theoretical Li^+ charge-balanced rings would diverge from the trend defined by the SiO_2 - $\text{NaAlSi}_3\text{O}_8$ glasses. In addition, the Li^+ cations are bonded to three O atoms rather than four as in the glasses, which leads to a stronger perturbation of the T-O-T linkages. In any case, our results do show that the frequency of the O_{br} breathing mode is a function of the type of charge-balancing cation (M) and the MAI content of the ring or glass.

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REFERENCES CITED

- Barrio, R.A., Galeener, F.L., Martinez, E., and Elliott, R.J. (1993) Regular ring dynamics in AX_2 tetrahedral glasses. *Physical Review B*, 48, 15672–15689.
- Bartsch, M., Bornhauser, P., Calzaferri, G., and Imhof, R. (1994) $H_2Si_4O_{12}$: A model for the vibrational structure of zeolite A. *Journal of Physical Chemistry*, 98, 2817–2831.
- Bates, J.B., Hendricks, R.W., and Shaffer, L.B. (1974) Neutron irradiation effects and structure of noncrystalline SiO_2 . *Journal of Chemical Physics*, 61, 4163–4176.
- Beran, S. (1982) Quantum chemical study of the physical characteristics of Mg faujasites and their interactions with water. *Zeitschrift für Physikalische Chemie Wiesbaden*, 130, 81–89.
- Casewit, C.J., Colwell, K.S., and Rappe, A.K. (1992) Application of a universal force field to main group compounds. *Journal of the American Chemical Society*, 114, 10046–10053.
- Chakoumakos, B.C., Hill, R.J., and Gibbs, G.V. (1981) A molecular orbital study of rings in silicates and siloxanes. *American Mineralogist*, 66, 1237–1249.
- Creighton, J.A., Deckman, H.W., and Newsam J.M. (1994) Computer simulation and interpretation of the infrared and Raman spectra of sodalite. *Journal of Physical Chemistry*, 98, 448–459.
- Dowty, E. (1991) ATOMS: A computer program for displaying atomic structures. Eric Dowty, Kingsport, Tennessee.
- Dutta, P.K., Rao, K.M., and Park, J.Y. (1991) Correlation of Raman spectra of zeolites with framework architecture. *Journal of Physical Chemistry*, 95, 6654–6656.
- Frisch, M.J., Trucks, G.W., Head-Gordon, M., Gill, P.M.W., Wong, M.W., Foresman, J.B., Johnson, B.G., Schlegel, H.B., Robb, M.A., Replogle, E.S., Gomperts, R., Andres, J.L., Raghavachari, K., Binkley, J.S., Gonzalez, C., Martin, R.L., Fox, D.J., Defrees, D.J., Baker, J., Stewart, J.J.P., and Pople, J.A. (1992) GAUSSIAN 92 Revision D2. Gaussian, Pittsburgh, Pennsylvania.
- Furakawa, T., Fox, K.E., and White, W.B. (1981) Raman spectroscopic investigation of the structure of silicate glasses: III. Raman intensities and structural units in sodium silicate glasses. *Journal of Chemical Physics*, 75, 3225–3237.
- Galeener, F.L. (1982a) Planar rings in glasses. *Solid State Communications*, 44, 1037–1040.
- (1982b) Planar rings in vitreous silica. *Journal of Non-Crystalline Solids*, 49, 53–62.
- Galeener, F.L., and Mikkelsen, J. (1981) Vibrational dynamics in ^{18}O -substituted vitreous SiO_2 . *Physical Review B*, 23, 5527–5530.
- Galeener, F.L., and Geissberger, A. (1983) Vibrational dynamics in ^{30}Si -substituted vitreous SiO_2 . *Physical Review B*, 27, 6199–6204.
- Galeener, F.L., Barrio, R.A., Martinez, E., and Elliott, R.J. (1984) Vibrational decoupling of rings in amorphous solids. *Physical Review Letters*, 53, 2429–2432.
- Garofalini, S.H. (1984) Defect species in vitreous silica: A molecular dynamics simulation. *Journal of Non-Crystalline Solids*, 63, 337–345.
- Geisinger, K.L., Gibbs, G.V., and Navrotsky, A. (1985) A molecular orbital study of bond length and angle variations in framework structures. *Physics and Chemistry of Minerals*, 11, 266–283.
- Glendening, E.D., Reed, A.E., Carpenter, J.E., and Weinhold, F. (1992) NBO Version 3.1. University of Wisconsin–Madison.
- Glidewell, C., Robiette, A.G., and Sheldrick, G.M. (1970) Gas-phase electron diffraction structure of tetrameric prosiloxane (H_2SiO)₄. *Journal of the Chemical Society, Chemical Communications*, 13, 931–932.
- Hemley, R.J., Mao, H.K., Bell, P.M., and Mysen, B.O. (1986) Raman spectroscopy of SiO_2 glass at high pressure. *Physical Review Letters*, 57, 747–750.
- Hill, J.-R., and Sauer, J. (1989) Harmonic force constants of the $H_2Si-O-AlH_3$ anion: A model of Si-O-Al bonds in aluminosilicates. *Zeitschrift für Physikalische Chemie Leipzig*, 270, S.203–206.
- (1994) Molecular mechanics potential for silica and zeolite catalysts based on ab initio calculations: 1. Dense and microporous silica. *Journal of Physical Chemistry*, 98, 1238–1244.
- Horkner, W., and Muller-Buschbaum, H.-K. (1976) Zur kristallstruktur von $CaAl_2O_4$. *Journal of Inorganic Nuclear Chemistry*, 38, 983–984.
- Humbert, B., Burneau, A., Gallas, J.P., and Lavalley, J.C. (1992) Origin of the Raman bands, D_1 and D_2 , in high surface areas and vitreous silicas. *Journal of Non-Crystalline Solids*, 143, 75–83.
- Kroll, H., and Ribbe, P.H. (1983) Lattice parameters, composition and Al,Si order in alkali feldspars. In *Mineralogical Society of America Reviews in Mineralogy*, 2, 57–99.
- Kubicki, J.D., and Sykes, D. (1993a) Molecular orbital calculations of vibrations in three-membered aluminosilicate rings. *Physics and Chemistry of Minerals*, 19, 381–391.
- (1993b) Molecular orbital calculations on $H_2Si_2O_7$ with a variable Si-O-Si angle: Implications for the high-pressure vibrational spectra of silicate glasses. *American Mineralogist*, 78, 253–259.
- (1995) Molecular orbital calculations on the vibrational spectra of Q^3 T-(OH) species and the hydrolysis of a 3-membered aluminosilicate ring. *Geochimica et Cosmochimica Acta*, 59, 4791–4797.
- Lasaga, A.C., and Gibbs, G.V. (1988) Quantum mechanical potential surfaces and calculations on minerals and molecular clusters. *Physics and Chemistry of Minerals*, 16, 29–41.
- McKeown, D.A., Galeener, F.L., and Brown, G.E., Jr. (1984) Raman studies of Al coordination in silica-rich sodium aluminosilicate glasses and some related minerals. *Journal of Non-Crystalline Solids*, 68, 361–378.
- McMillan, P.F., and Graham, C.M. (1981) The Raman spectra of quenched albite and orthoclase glasses from 1 atm to 40 kb. In C.E. Ford, Ed., *Progress in experimental petrology, fifth progress report of research supported by N.E.R.C.*, p. 112–115. Natural Environment Research Council Publications Series D, no. 18. Eaton, Wallasey, U.K.
- McMillan, P.F., Piriou, B., and Navrotsky, A. (1982) A Raman study of glasses along the joins silica-calcium aluminate, silica-sodium aluminate, and silica-potassium aluminate. *Geochimica et Cosmochimica Acta*, 46, 2021–2037.
- McMillan, P.F., Piriou, B., and Couty, R. (1984) A Raman study of pressure-densified silica. *Journal of Chemical Physics*, 81, 4234–4236.
- Muller, D., Gessner, W., Samoson, A., Lippmaa, E., and Scheler, G. (1986) Solid-state ^{27}Al NMR studies on polycrystalline aluminates of the system $CaO-Al_2O_3$. *Polyhedron*, 5, 779–785.
- Nicholas, J.B., Winans, R.E., Harrison, R.J., Iton, L.E., Curtiss, L.A., and Hopfinger, A.J. (1992) Ab initio molecular orbital study of the effects of basis set size on the calculated structure and acidity of hydroxyl groups in the framework molecular sieves. *Journal of Physical Chemistry*, 96, 10247–10257.
- O’Keeffe, M. and Gibbs, G.V. (1984) Defects in amorphous silica: Ab initio MO calculations. *Journal of Chemical Physics*, 81, 876–879.
- Pople, J.A., Schlegel, H.B., Krishnan, R., Defrees, D.J., Binkley, J.S., Frisch, M.J., Whiteside, R.A., Hout, R.F., and Hehre, W.J. (1981) Molecular-orbital studies of vibrational frequencies. *International Journal of Quantum Chemistry: Quantum Chemistry Symposium*, 15, 269–278.
- Reed, A.E., Curtiss, L.A., and Weinhold, F. (1988) Intermolecular interactions from a natural bond orbital, donor-acceptor viewpoint. *Chemical Reviews*, 88, 899–926.
- Revesz, A., and Walrafen, G. (1983) Structural interpretations for some Raman lines from vitreous silica. *Journal of Non-Crystalline Solids*, 54, 323–333.
- Ribbe, P.H., Ed. (1983) *Feldspar mineralogy*, 362 p. Mineralogical Society of America, Washington, DC.
- Roy, B., and Navrotsky, A. (1984) Thermochemistry of charge-coupled substitutions in silicate glasses: The systems $M_{7/8}AlO_2-SiO_2$ (M = Li, Na, K, Rb, Cs, Mg, Ca, Sr, Ba, Pb). *Journal of the American Ceramic Society*, 67, 606–610.
- Sauer, J. (1989) Molecular models in ab initio studies of solids and surfaces: From ionic crystals and semiconductors to catalysts. *Chemical Reviews*, 89, 199–255.
- Sauer, J., and Hill, J.R. (1994) The acidity of surface silanol groups: A

- theoretical estimate based on ab initio calculations on a model surface. *Chemical Physics Letters*, 218, 333–337.
- Seifert, F., Mysen, B.O., and Virgo, D. (1982) Three-dimensional network structure of quenched melts (glass) in the systems $\text{SiO}_2\text{-NaAlO}_2$, $\text{SiO}_2\text{-CaAl}_2\text{O}_4$ and $\text{SiO}_2\text{-MgAl}_2\text{O}_4$. *American Mineralogist*, 67, 696–717.
- Sharma, S.K., Virgo, D., and Mysen, B.O. (1978) Structure of melts along the join $\text{SiO}_2\text{-NaAlSiO}_4$ by Raman spectroscopy. *Carnegie Institution of Washington Year Book*, 77, 652–658.
- Sharma, S.K., Mammone, J.F., and Nicol, M.F. (1981) Raman investigation of ring configurations in vitreous silica. *Nature*, 292, 140–141.
- Sharma, S.K., Philpotts, J.A., and Matson, D.W. (1985) Ring distributions in alkali- and alkaline-earth aluminosilicate framework glasses: A Raman spectroscopic study. *Journal of Non-Crystalline Solids*, 71, 403–410.
- Sharma, S.K., Yoder, H.S., and Matson, D.W. (1988) Raman study of some melilites in crystalline and glassy states. *Geochimica et Cosmochimica Acta*, 52, 1961–1967.
- Titova, T.I., Kosheleva, L.S., and Kosslick, H. (1995) IR lattice vibrational study on Mg-containing zeolite A. *Journal of Molecular Structure*, 349, 473–478.
- Tossell, J.A. (1993) A theoretical study of the molecular basis of the Al avoidance rule and of the spectral characteristics of Al-O-Al linkages. *American Mineralogist*, 78, 911–920.
- Wainwright, J.E., and Starkey, J. (1971) A refinement of the structure of anorthite. *Zeitschrift für Kristallographie*, 133, 75–84.

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